VIII. *On the Insulation of Fluorine.* *By* George James Knox, Esq., A.M., M.R.I.A., and the Rev. Thomas Knox, M.R.I.A.

Read 10th April, 1837.

THE composition of hydro-fluoric acid had been a subject of discussion among chemists until the year 1810, when M. Ampere, from considering the analogy which subsisted between this acid and muriatic, was led to draw similar conclusions with respect to the composition of each. Sir Humphry Davy was at first opposed to these views, but on further consideration, being led to change his opinion, he brought forward experimental proofs of their correctness, which may be found in the Philosophical Transactions.*

Having by these experiments demonstrated the probable existence of fluorine, he proceeded to other experiments with the view of obtaining it in an insulated state; for which purpose he heated fluoride of mercury and fluoride of silver in glass vessels, filled with chlorine; he obtained chloride of silver from the one, and corrosive sublimate from the other; and the vessels were found to be filled with fluosilicic acid and oxygen arising from the decomposition of the silica by the nascent fluorine. He obtained similar results when fluoride of potassium and fluoride of sodium were heated with chlorine.

When the same experiments were repeated in vessels of platinum and silver, the vessels were powerfully acted upon. In glass vessels, coated with cuprane and horn-silver, the chlorides were fused at the temperature required for the experiments, and the glass was acted on as before. In a platinum vessel coated with fluoride of potassium, a gas was obtained having an odour more disagreeable than that of chlorine; but the platinum was found to have been acted upon. Sir H. Davy made many other experiments with the view of decomposing hydro-fluoric acid by means of chlorine and oxygen, by passing these gases with the

* Phil. Trans. 1813, p. 263.

vapour of hydro-fluoric acid through a platinum tube heated red hot; and by distilling it from salts containing abundance of oxygen or of chlorine. He distilled also the fluorides of lead and mercury with phosphorus and sulphur in glass tubes, with the formation of a phosphuret and sulphuret, and action on the glass; when the glass tubes were lined with sulphur, a limpid liquid condensed in a part of the tube cooled to zero.

From these experiments he concludes, that there exists in the fluoric compounds a peculiar element, possessed of strong attraction for metallic bodies and hydrogen, which from the low refractive power of hydro-fluoric acid, he supposed would have less refractive power than any substance known, possessing at the same time higher acidifying and saturating powers than either oxygen or chlorine, and which, when obtained in an insulated state, would prove to be a gas.

We understand that Sir H. Davy got vessels of fluor-spar made for the purpose of repeating these experiments, but since he has not published any which he may have tried with them, we conclude that he either did not employ them, or that they did not conduct him to any new results.

Such was the state of the subject till the year 1836, in the spring of which year we commenced the following investigation. Sir H. Davy's experiments having shown that chlorine would decompose fluoride of mercury in glass vessels, it became a question to determine whether the same result would take place in vessels upon which the nascent fluorine could exert no action. This we tried by heating dry chlorine with fluoride of mercury in two small perforated crystals of fluor spar. A chloride of mercury was formed. Then, in small vessels of fluor-spar containing chlorine, we heated fluorides of mercury, lead, and hydrofluate of ammonia; in the first were formed crystals of corrosive sublimate; in the second the fluoride of lead was not acted upon; and the last vessel was filled with vapour of hydro-fluoric acid. We then procured fluor-spar vessels of a larger size, lapped with wire, for the purpose of equalizing the temperature, and so preventing the vessels from splitting on a sudden application of heat. Instead of a flat cover for the vessels we had fluor-spar receivers made, the cavities of which were filled with ground-stoppers of fluor. On moving the receivers over the mouth of the vessel the stoppers fall in, and their places in the receivers are occupied by whatever the contents of the vessel may be. On the top of these vessels were three or four small depressions, in which were placed any substances that we wished to submit to the action of the gas, and over which the re-

ceivers, when filled with the gas, could be slid. The results we came to with these vessels were the following:—Litmus paper was reddened, glass strongly acted upon, gold on one occasion slightly acted upon, owing, as we believe, to the formation of a fluoride of gold, as we were led to suppose by the action of the product on glass, when heated with sulphuric acid. From having ascertained the perfect dryness of the materials, and from the absence of moisture when the cover had been cooled down by the evaporation of sulphuret of carbon, we proved the absence of hydro-fluoric acid; and from having obtained bi-chloride of mercury, we inferred the disengagement of fluorine. These reasons alone, we conceived, would have been sufficient to justify us in supposing the insulation of fluorine.

It may be mentioned here, that after we had entered on our investigations, we met with a notice of some experiments made by M. Baudrimont, with the intention of insulating fluorine in glass vessels. He heated a mixture of fluor-spar and peroxide of manganese with sulphuric acid in a glass retort, and collected in a dry glass vessel a gas of a yellowish brown colour, which bleached litmus paper, and acted upon gold in the cold, differing from the gas that we have obtained in these qualities.

In the month of December last we had other fluor vessels constructed at Mawe's establishment, of a similar form to those already employed, but much larger size; they were lapped with fine iron wire, were of a very considerable thickness, and could contain about four fluid ounces; the upper part of these vessels was turned round, and reduced in thickness, so as to fit into a flat slab of fluor-spar, and the upper edge of the vessels was then polished off, so as to be on the same level with the flat slab, which acted as a table upon which the covers of the vessels and the receivers for the gas could be slid, without letting the contents mix with the atmospheric air. The receivers for the gases were square, about two inches and a half high, and one and a quarter wide, and the interior, which was circular, and about five-eighths of an inch in diameter, was fitted with a stopper of fluor. On opposite sides of these receivers (*see Plate*) holes were drilled quite through, intersecting the former cavity at right angles, and into these holes were fitted, air-tight, clear crystals of fluor, so that the colour of any gas in the receiver could be distinctly observed on looking through them. There were some small depressions in the flat slab, which we have above called *the table*, in which might be placed any piece of metal or other substance

on which it might be wished to try the effect of the gas; one edge of the table was straight, so that a receiver full of gas could be removed on a slab of fluor without loss of the contents. The mode of using these vessels is as follows:—after the vessel with its contents has been heated gradually, so as to raise the temperature, and expel the water from the fluoride to be acted on, it is filled with dry chlorine, and a receiver is fastened down upon it with a weight or clamp; then the apparatus being heated to any temperature required, when we wish to examine the gas in the receiver, a second receiver, with a stopper in its cavity, is placed beside the first, and is slid on the table, till it occupies the place of the first; its stopper then falls into the vessel, and its cavity is filled with gas. This receiver, in like manner, is replaced by another, and so on till the vessel has been choked up with stoppers. The contents of the receivers can then be examined by being slid over various tests in the places made for that purpose on the surface of the table. The entire apparatus is supported on a stand over a lamp.

In recommencing the experiments in these new vessels, adapted for showing the colour of the gas in the manner above described, we found that when perfectly pure fluoride of mercury was used, the gas obtained was colourless; and to the upper part of the vessel inside, were suspended feathery crystals of corrosive sublimate. The gas obtained in the receivers has a heavy smell, not pungent or irritating, and thereby easily distinguishable from chlorine or hydro-fluoric acid. When exposed to the air it does not fume, which would be the case were the latter of these present.

With regard to its power of supporting combustion, red-hot wire appeared to become slightly brighter, but did not scintillate; we tried it also with burning charcoal and phosphorus, which latter was not extinguished; but these effects were very slight, and cannot be relied on as certain, as the atmospheric air must be admitted in plunging in the heated wire.

We attempted its detonation with hydrogen, thinking thereby to obtain hydro-fluoric acid. For this purpose we inserted two platinum wires through the opposite sides of a fluor-spar receiver, upon which, when filled with dry hydrogen, we placed a receiver of the gas obtained in the vessels. On passing a spark from a Leyden jar, detonation took place; there was an absorption, and on separating the vessels slight fumes appeared, from which we inferred that hydro-fluoric acid

had been formed; but in moving the vessels over each other some air may have got in, which would account for the detonation. This was repeated frequently; but, from the nature of the manipulation, the result could not be depended on. On collecting and examining the gas that remained on one occasion, after detonation, there was no hydrogen found.

On placing many receivers filled with the gas in succession over water, whether hot or cold, the solution, if such, had all the properties of hydro-fluoric acid in acting on glass, reddening litmus, and giving precipitates with lime and barytes.

We passed some through hot water into a graduated glass tube. There was a considerable absorption, and a deposit of flakes of silica. The remaining gas, on examination, proved to be atmospheric air, with some oxygen. The admission of some atmospheric air in the transference is, from the nature of the vessels, almost unavoidable, for which reason the results must be received with caution.

When a receiver of the gas is placed over dry litmus and Brazil wood-papers, the former is reddened, the latter turned yellow, and *in no instance* were they ever bleached. When a receiver was placed over wet glass it was strongly acted upon. When the glass was carefully dried there was less action than before. From which circumstance, supposing that if the glass were perfectly dry, there would be no action upon it, we placed a small piece in a perforation in the interior of the receiver, and found it was still acted on, but not more so than when fluoride of mercury alone was in the vessel.

In trying the action on the metals we found it necessary to try the separate action of hydro-fluoric acid and sublimed fluoride of mercury, in order to distinguish the action that might be due to fluorine alone, from that which might be caused by their presence. Corrosive sublimate also, when in vapour, acts powerfully in many cases, and these two last substances must necessarily be always present. The hydro-fluoric acid was formed in the vessels themselves.

The results given in the following table, in the column headed Fluorine, are those which were produced on the various metals, over which a receiver, full of the gas, obtained in the usual way, had been placed.

The Action on the various Metals by Fluorine, Hydro-fluoric Acid, and Vapour of Fluoride of Mercury.

	Fluorine.	Hydro-fluoric Acid.	Vapour of Fl. of Mercury.	OBSERVATIONS.
Gold	Action.	None.	None.	The action on gold was only obtained *once*, and that in the small vessels when greater heat was applied. The action was not obtained on the palladium without allowing the gas to act for some hours on it. Corrosive sublimate, at the heat applied, acts on antimony, though not on bismuth; so that bismuth, palladium, and, at high temperature, gold, seem to be the only metallic tests of the existence of the gas in the receivers.
Platinum . . .	None.	None.	None.	
Palladium . . .	Action.	None.	None.	
Rhodium . . .	None.	None.	None.	
Silver	Action.	Action.	Action.	
Mercury	Action.	Action.	Action.	
Lead	Action.	Action.	Action.	
Cadmium . . .	Action.	Action.	Action.	
Copper	Action.	Action.	Action.	
Bismuth	Action.	None.	None.	
Antimony . . .	Action.	None.	None.	
Iron	Action.	Action.	Action.	
Zinc	Action.	Action.	Action.	
Tin	Action.	Action.	Action.	

It is right to state here, that the action on the palladium and bismuth was not proved to be from the formation of fluorides of those metals, in consequence of the minuteness of the pieces used. That on the gold we have since confirmed by the action upon it by the battery.

In order to determine the relative attraction of fluorine for those metals upon which it does not seem to act except in the nascent state, we made platinum, palladium, gold, and rhodium successively constitute the positive pole of a battery of sixty pair of plates, electrolizing moistened fluoride of lead. The platinum was covered with a chocolate-coloured substance, which disappeared on heating. The action on the palladium gave rise to a reddish-brown colour, the same as that obtained before by the direct action of the gas. The gold was only occasionally acted upon,—the colour, brownish-red. The rhodium was never acted upon in the trials we gave it; so that if this should be confirmed, fluorine might probably be obtained in an insulated state by electrolizing a fluoride, using rhodium as the positive pole.

We repeated M. Baudrimont's experiments in glass, and in the vessels of fluor spar, but were unable to obtain a coloured gas having the properties which he describes. From the nature of his experiments, we conceive it to be impossible that the gas obtained by M. Baudrimont could be fluorine, on account of

the water present, and consider it probable that it was a fluoride of oxygen formed by the union of the nascent oxygen and fluorine. To determine this, we heated in a dry glass tube a mixture of iodic acid and fluoride of mercury, supposing that when the iodine decomposed the fluoride of mercury, fluorine and oxygen being set free from their combinations with oppositely electrical bodies (mercury and iodine) would be in the most favourable condition for combining. On applying a moderate heat a yellow gas arose, which did not act on the glass, and bleached litmus paper slightly; on increasing the temperature, the yellow iodide of mercury sublimed, then iodine, and finally fluoride of mercury.

We have to remark, with regard to our present mode of manipulating, that about 100 grains of the fluoride of mercury is a sufficient quantity; but that its *absolute dryness* must be ascertained, which may be known by its subliming plentifully out of the mouth of the vessel. It requires about two hours to effect this, and to raise the temperature of the fluor vessel sufficiently high previous to passing in the chlorine. When filled with the chlorine, which must be also well dried, we apply the heat of Rose's spirit lamp, with circular wick, for about twenty minutes, which we find to be always sufficient for the decomposition of the fluoride. When we have examined the contents of the vessel, after a quarter of an hour, we have found chlorine in it, but *never* when it has been heated the above length of time. If, instead of drying the material perfectly, it happened that a trace of moisture was allowed to remain, then, instead of the usual result, we obtained copious fumes of hydro-fluoric acid.

In conclusion, we beg to state, that we are far from wishing it to be supposed that we consider the doubts on the nature of fluorine set at rest by the foregoing researches. But we think ourselves justified, from the experiments we have detailed, to conclude, that some advances have been made, and that a mode of operating on that element has been pointed out, which may be successfully employed hereafter, and which, in other hands, may lead to more complete results.

EXPLANATION OF PLATE.

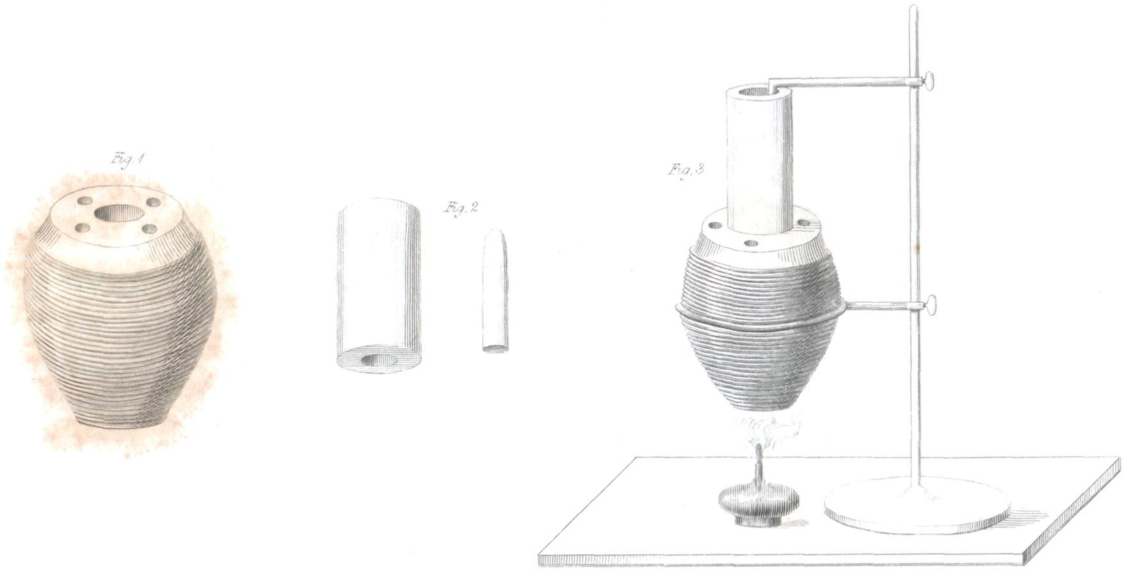
FIRST SET OF VESSELS, ONE-HALF OF THE ACTUAL SIZE.

Fig. 1.—The vessel.
Fig. 2.—Receiver and its stopper.
Fig. 3.—The whole, together with lamp, as when in use.

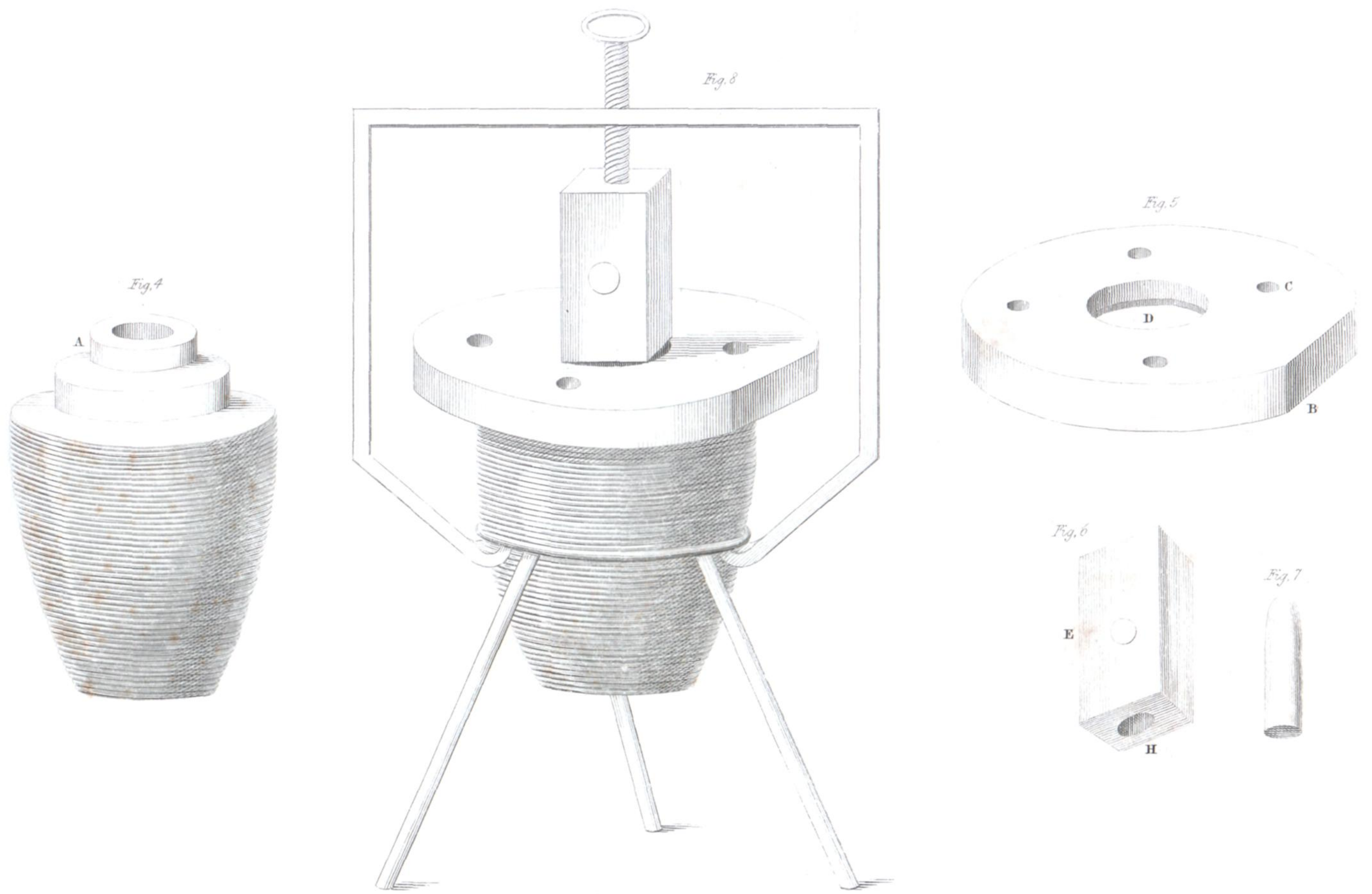
SECOND SET OF VESSELS, ONE-THIRD OF ACTUAL SIZE.

Fig. 4.—The vessel.
 A.—The shoulder on which the table rests.
Fig. 5.—The table.
 B.—The flat edge.
 C.—The small depressions.
 D.—Aperture in centre, through which the top of vessel is inserted.
Fig. 6.—The receiver.
 E.—The clear piece inserted in the side.
 H.—The aperture in which the stopper fits.
Fig. 7.—The stopper.
Fig. 8.—The whole apparatus, when put together on a tripod, with the receiver fastened down by a clamp.

First set of vessels, one half the actual size.



Second set of vessels, one third of actual size.



J. Kirkwood Sc.